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認 証

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証 明

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平成16年 5 月 12 日

東京法務局長

石井政治



# APOSTILLE

(Convention de La Haye du 5 octobre 1961)

1. Country: JAPAN

This public document

2. has been signed by **TOICHI FUJIWARA**

3. acting in the capacity of Notary of the Tokyo Legal Affairs Bureau

4. bears the seal/stamp of **TOICHI FUJIWARA**

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5. at Tokyo

6. **MAY 12 2004**

7. by the Ministry of Foreign Affairs

8. 04- N<sup>o</sup> 002444

9. Seal/stamp:

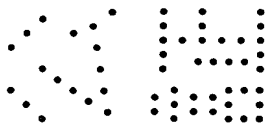
10. Signature



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For the Minister for Foreign Affairs



Registration No. 713

DECLARATION

I, Yuki MIYAKE residing at 1223-1 A-409, Sonno-cho, Inage-ku, Chiba-shi, Chiba, 263-0051, Japan do hereby solemnly and sincerely declare:

1. That I am an employee of Furuya & Co. located  
at Hamacho-Hanacho Building, 2-17-8, Nihonbashi-Hamacho, Chuo-ku,  
Tokyo 103-0007, Japan,
2. That I am well acquainted with the Japanese and English  
languages, and
3. That the attached English document is a true and correct translation into  
English of the certified copy of the Japanese patent application No. 6-  
318549 filed on 21 December 1994, a copy of which is hereto attached.

And I make this solemn declaration conscientiously  
believing the same to be true and correct.

on the date of 12 May 2004

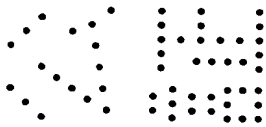
三宅有紀

By Yuki MIYAKE  
This is to certify that this document  
was subscribed before me by the above-named  
person(s) on this day.



MAY 12 2004

  
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NOTARY



Patent Office  
Japanese Government

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application: 21 December 1994

Application Number: patent application No. 6-318549

Applicant(s): Daicel Chemical Industries, Ltd.

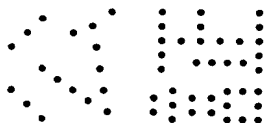
dated 5 January 1996

Commissioner

Patent Office

Mr. Yuji KIIYOKAWA

Shusho No.  
Shushotokuhei 07-3078266



[Designation of Document] Patent Application

[Reference Number] 194DK104

[Application Date] 21 December 1994

[Addressee] the Commissioner of the Patent Office

[IPC] C06D 5/06

[Title of the Invention] Gas Generant Composition

[Number of Claims] 8

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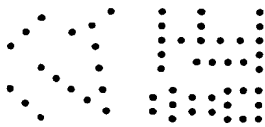
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[Designation of the Payment]

[Way of Payment] prepayment

[Number of the Deposit] 010685

[Amount of the Payment] 21,000

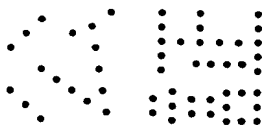
[List of the Exhibit]

[Name of the Subject] Specification 1

[Name of the Subject] Abstract 1

[Number of the General Power of Attorney] 9005922

[Request of the proof] yes



JP6-318549

[Designation of Document] Specification

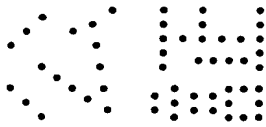
[Title of the Invention] Gas Generant Composition

[Claims]

[Claim 1] A gas generant composition having, as the essential components, a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer, which comprises a molybdenum oxide catalyst of at least one selected from the group consisting of molybdenum dioxide, molybdenum trioxide, molybdic acid and ammonium molybdate.

[Claim 2] The gas generant composition according to claim 1, which further comprises, as a decomposition promoter for nitrogen-containing organic compound, at least one of oxides, chlorides and carbonates of an element selected from the group belonging to Groups I, II, III, IV, V, VI (except molybdenum), VII and VIII of the periodic table.

[Claim 3] The gas generant composition according to claim 2, wherein oxides, chlorides and carbonates of an element selected from the group belonging to Groups I, II, III, IV, V, VI (except molybdenum), VII and VIII of the periodic table are oxides, chlorides or carbonates of boron, cerium, barium, calcium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, titanium, antimony, lead or ytterbium.



[Claim 4] The gas generant composition according to any one of claims 1 to 3, wherein the nitrogen-containing organic compound is at least one selected from the group consisting of organic compounds containing amino group or amido group and tetrazole derivatives.

[Claim 5] The gas generant composition according to claim 4, wherein the organic compound containing amino group or amido group is azodicarbonamide.

[Claim 6] The gas generant composition according to claim 4, wherein the tetrazole derivative is aminotetrazole.

[Claim 7] The gas generant composition according to any one of claims 1 to 6, wherein the oxygen-containing inorganic oxidizer is at least one selected from the group consisting of potassium nitrate, strontium nitrate and potassium perchlorate.

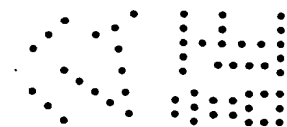
[Claim 8] The gas generant composition according to any one of claims 1 to 6, wherein the oxygen-containing inorganic oxidizer is a mixture of strontium nitrate and potassium perchlorate.

#### [Detailed Description of the Invention]

[0001]

#### [Field of Industrial Application]

The present invention relates to a gas generant composition. More specifically, the invention relates to a non-azide type gas generator composition which supplies gas components by burning for the purpose of inflating an air bag system.



[0002]

[Prior Art]

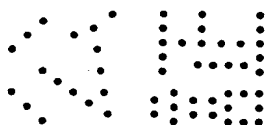
In the event of collision of vehicles like cars at high speed, the driver and passengers might be injured or killed by clashing against internal hard or dangerous parts of the vehicles such as the handle and front glass. In order to prevent such disasters, air bag systems for automobiles have been developed which inflate quickly by a gas generated from a gas generant.

Requirements for the gas generant of an automobile air bag system are very severe. At first, the bag should inflate in a very short period of time, usually not longer than 40 to 50 milliseconds. Further, The atmosphere within the bag is most suitable when it corresponds to the air composition in the car. These requirements are satisfied by gas generants which have been currently used in common comprising a base gas generant such as alkali metal salts (in particular sodium azide) or alkaline earth metal salts of hydrazoic acid. However, these gas generants are seriously defective in that the main component, sodium azide is toxic and that the by-products alkali components are also toxic. Hence, environmental pollution brought by a large amount of scrap cars and health hazard of the driver and passengers when the gas is generated are concerned.

[0003]

For the purpose of overcoming these problems, non-azide type gas

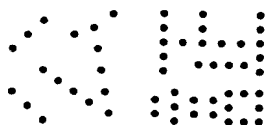




generants have been under development in place of sodium azide type. For example, JP-A 3-208878 discloses a composition which comprises a main component of oxygen-containing oxidizer such as tetrazole, triazole, or their metal salts combined with ammonium perchlorate or sodium nitrate and an auxiliary component of a metal oxide such as  $V_2O_5$ ,  $CuO$  or  $Fe_2O_3$ . The metal oxide mentioned forms a solid combustion product, which is easily removed by filtration when undesired components are removed by filtration prior to release the formed gas into the bag in an air bag system, and converts CO which is toxic to human bodies generated from the nitrogen-containing organic compound to  $CO_2$ . JP-B 64-6156 and JP-B 64-6157 disclose a gas generant which contains, as the main component, a metal salt of bitetrazole compound that does not contain hydrogen. JP-A 3-208878 further discloses a gas generant having a transition metal complex of aminoarazole as the main component. These non-azide type compounds disclosed in the series of prior art references are characteristic in that the concentration of carbon monoxide released is low since the carbon number in the one molecule is small; however, the amount of nitrogen oxides, toxic to human bodies, increases in all the cases and the performance is not satisfactory in respect of the inflation period of the bag.

[0004]

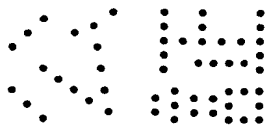
[Problems to be Solved by the Invention]



The present inventors previously had found that a non-azide type gas generant having a nitrogen-containing organic compound such as azodicarbonamide and a certain inorganic oxygen-containing oxidizer as the effective component is free from environmental pollution, satisfactory in respect of the inflation period of the bag, and advantageous in the cost, and filed the patent applications (with reference of JP-A 4-185251, JP-A 4-185253 and JP-A 5-18782).

[0005]

In the combustion of an organic compound containing oxygen, it is well-known that carbon monoxide will generate as incomplete combustion product even when an oxidizer is used in an amount exceeding the chemical equivalence that releases the necessary amount of oxygen for burning combustible elements, such as carbon, hydrogen and others, in the organic compound. In view of this fact, the nitrogen compound, such as azodicarbonamide, used as the main agent in the mentioned gas generant is supposed to release a relatively rather large amount of carbon monoxide and nitrogen oxides, and a trace of NO<sub>x</sub> which contains a little amount of nitrogen is produced as a by-product since many carbon atoms are contained per molecule. For the purpose of avoiding such by-product carbon monoxide, use of a catalyst may be possible which convert carbon monoxide to carbon dioxide. Many components are known for such catalysts as written in a book "Classified Table for Catalysts depending on Reaction, Vol. I" edited by Tarama et al. of Kyoto University and published by Kagaku Kogyo-sha



(in Page 291-292). However, no catalysts are known that are generally reactive enough in a contact period of time of several dozens milliseconds as required for a gas generant for air bag system;  $V_2O_5$ ,  $CuO$ ,  $Fe_2O_3$  and other metal oxides are used at present in spite of their low activity. And, such a catalyst that decomposes  $NO_x$  without a reducing agent is hardly known.

[0006]

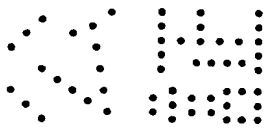
[Means to Solve the Problem]

Further, as a result of intensive studies of the present inventors, it has been surprisingly found that a certain molybdenum oxide catalyst has an important function for decreasing carbon monoxide and nitrogen oxides; this finding has lead to completion of the present invention.

According to the third embodiment of the present invention, a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components is provided, which composition is characterized by containing a molybdenum oxide catalyst comprising at least one selected from the group consisting of molybdenum dioxide, molybdenum trioxide, molybdic acid and ammonium molybdate.

[0007]

The gas generant composition of the present invention contains a nitrogen-containing organic compound and a oxygen-containing

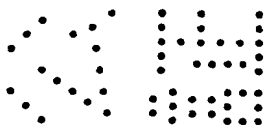


inorganic oxidizer as the essential components.

There is no particular limitation for the nitrogen-containing organic compound usable for the present invention provided that nitrogen atom is contained in the molecule; examples of the nitrogen-containing organic compound include organic compounds containing amino group or amido group and tetrazole derivatives. Specific examples of the organic compounds containing amino group or amido group include: azodicarbonamide, urea, aminoguanidine bicarbonate, biuret, dicyandiamide, and hydrazides; preferably azodicarbonamide. Specific examples of the tetrazole derivatives include: aminotetrazole, tetrazole, azotetrazole, bitetrazole, tetrazole carboxylate, their alkali metal salts and their alkaline earth metal salts; and preferably aminotetrazole. The nitrogen-containing organic compound may be used in single or as a mixture of two or more kinds.

[0008]

The oxygen-containing inorganic oxidizer usable in the present invention may be selected widely from known ones such as nitrates, nitrites, and oxyhalogenates. Specific examples of the oxygen-containing inorganic oxidizer include potassium nitrate, sodium nitrate, strontium nitrate, potassium nitrite, sodium nitrite, sodium perchlorate, potassium perchlorate, sodium chlorate, and potassium chlorate. More specifically, a single compound or mixture selected from  $\text{KNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$  and  $\text{KClO}_4$  may be used; a mixture of  $\text{Sr}(\text{NO}_3)_2$



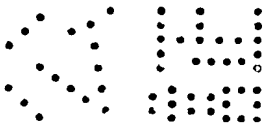
and  $\text{KClO}_4$  is preferable in particular.

[0009]

The blend ratio of the nitrogen-containing organic compound to oxygen-containing inorganic oxidizer in the gas generant composition of the present invention may be optionally selected depending on the combustion rate, combustion temperature and combustion temperature, although the ratio is normally selected so as to be stoichiometric when the nitrogen-containing organic compound is completely oxidized and burned on the basis of the oxygen amount. For example, about 20 through 400 parts by weight of the oxygen-containing inorganic oxidizer is blended with 100 parts by weight of the nitrogen-containing organic compound; blending some excess amount of the oxygen-containing inorganic oxidizer compared to the stoichiometric amount for complete combustion is preferred for enhancing the efficiency of molybdenum oxide catalyst provided that the gas generation efficiency based on the unit weight of the gas generant composition is not substantially lowered.

[0010]

According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, a molybdenum oxide catalyst of at least one selected from the group consisting of molybdenum dioxide, molybdenum trioxide, molybdic acid and ammonium molybdate, is further blended. The molybdenum oxide



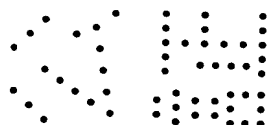
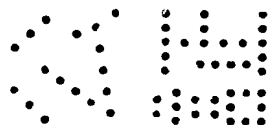
type catalyst mentioned above can be produced by a process known to the art.

[0011]

In the present invention, the content of molybdenum oxide catalyst is not limited, but normally 1 through 40% by weight or 1 through 30% by weight, preferably 3 through 30% by weight or 3 through 20% by weight, and more preferably 3 through 20% by weight or 3 through 10% by weight, of the total weight of the composition that includes the gas generant containing the nitrogen-containing organic compound and oxygen-containing inorganic oxidizer as the essential components and the third component to be blended as mentioned above. Too much molybdenum oxide catalyst content is not desirable because the amount of generated gas is decreased against unit weight of the gas generant composition; and too little content is not desirable because the effect of decreasing toxic gas concentration is unsatisfactory.

[0012]

In the present invention, together with the above molybdenum oxide catalyst, at least one of oxides, chlorides and carbonates of an element selected from the group belonging to Groups I, II, III, IV, V, VI (except molybdenum), VII and VIII of the periodic table can be used as a decomposition promoter for nitrogen-containing organic compound. Examples of such oxides, chlorides and carbonates include oxides, chlorides or carbonates of boron, cerium, barium, calcium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, titanium,



antimony, lead or ytterbium. Specifically, they are  $B_2O_3$ ,  $Co_3O_4$ ,  $NiO$ ,  $CuO$ ,  $ZnO$ ,  $ZnCO_3$ ,  $MnO_2$ ,  $FeCl_3$ ,  $Pb_3O_4$ ,  $PbO_2$ ,  $PbO$ ,  $Sb_2O_3$ ,  $TiO_2$ ,  $V_2O_5$ ,  $CeO_2$ ,  $Ba_2O_3$ ,  $CaO_2$ , and  $Yb_2O_3$ . Most preferable is  $CuO$ .

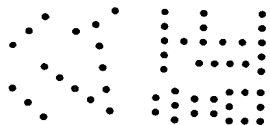
When at least one of oxides, chlorides and carbonates of an element selected from the group belonging to Groups I, II, III, IV, V, VI (except molybdenum), VII and VIII of the periodic table is used additionally, the content is preferably from 1 to 30% by weight of the composition of the present invention.

[0013]

For the purpose of enhancing the shaped strength of the gas generant composition, a binder, a decomposition promoter of nitrogen-containing organic compound, silica or the like may be blended. Examples of the binder include: fine crystal cellulose binders such as marketed under the trade name "Avicel"; polymer binders such as poval; organic binders such as starch; and inorganic binders such as silica sol, alumina sol and zirconia sol. An example of the organic decomposition promoter of nitrogen-containing organic compound includes urea.

[0014]

The composition according to the present invention is prepared by blending respective components mentioned above; resulting blended composition may be used as such for a gas generant, however, a formulated form is preferable. Any known methods are applicable for the formulation, and a suitable binder may be selected. Shape of the



formulated composition is not limited specifically and may be, for example, pellet, disc, ball, like-confetti, and like-tetrapod. The formulated composition may be without holes or with holes (such as briquette with holes or ring shape).

[0015]

[Effect of the Invention]

According to the present invention, in a gas generant composition containing a nitrogen-containing organic compound and an oxygen-containing inorganic oxidizer as the essential components, toxic components in the released gas, in particular carbon monoxide and nitrogen oxides, can be reduced to a practical level which is acceptable as an air bag system for automobile.

[0016]

[Examples]

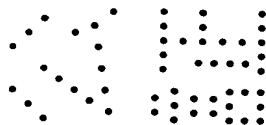
Now, the present invention is explained more specifically concerning the first to fifth embodiments by way of examples; however, the present invention is not limited to these examples if not out of the scope and spirit of the invention.

Hereinafter, a blending ratio and concentration in the following examples and comparative examples are based on weight ratio unless otherwise specified.

[0017]

Example 1



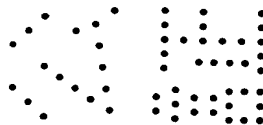


Powders consisting of 36 parts of azodicarbonamide, 32 parts of potassium perchlorate, 32 parts of strontium nitrate, and 20 parts of molybdenum trioxide were blended well; furthermore, an amount of 5% aqueous solution to be resulted to 0.2 parts of poval was added therewith. Resulting humid fine particles were adjusted to suitable fineness and water content for shape formulation, and formed into pellets (9.7 mm $\phi$  diameter x 4 mm) by pressing at a pressure of about 120 kg/cm<sup>2</sup> using a hydraulic tabletting machine. The pellets were subjected to a predetermined tank test (as described in JP-B 52-3620 and JP-B 64-6156) using a burning device equipped with a filter and coolant; thereby, the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank was evaluated. The burning pressure and period were of desired values. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.6% by gas chromatography. The nitrogen oxides were 200 ppm as determined by a detector tube.

[0018]

#### Example 2

Example 1 was repeated except 20 parts of molybdic acid was used in place of the 20 parts of molybdenum trioxide to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.4% by gas



chromatography. The nitrogen oxides were 180 ppm as determined by a detector tube.

[0019]

#### Example 3

Example 1 was repeated except 20 parts of ammonium molybdate was used in place of the 20 parts of molybdenum trioxide to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.5% by gas chromatography. The nitrogen oxides were 100 ppm as determined by a detector tube.

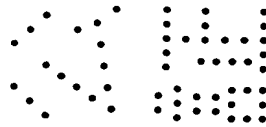
[0020]

#### Comparative Example 1

Example 1 was repeated except that the 20 parts of molybdenum trioxide was not used to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 2.3% by gas chromatography. The nitrogen oxides were not less than 2,000 ppm as determined by a detector tube.

[0021]

#### Example 4



Example 1 was repeated except 20 parts of molybdenum trioxide was replaced by 10 parts of copper oxide and 10 parts of molybdenum trioxide to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.7% by gas chromatography. The nitrogen oxides were 320 ppm as determined by a detector tube.

[0022]

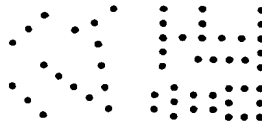
#### Example 5

Example 1 was repeated except 20 parts of molybdenum trioxide was replaced by 10 parts of copper oxide and 10 parts of molybdic acid to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.6% by gas chromatography. The nitrogen oxides were 270 ppm as determined by a detector tube.

[0023]

#### Example 6

Example 1 was repeated except 20 parts of molybdenum trioxide was replaced by 10 parts of copper oxide and 10 parts of ammonium molybdate to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period



were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 0.5% by gas chromatography. The nitrogen oxides were 230 ppm as determined by a detector tube.

[0024]

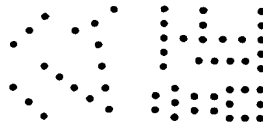
#### Comparative Example 2

Example 1 was repeated except 20 parts of molybdenum trioxide was replaced by 10 parts of copper oxide to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 1.5% by gas chromatography. The nitrogen oxides were not less than 2,000 ppm as determined by a detector tube.

[0025]

#### Comparative Example 3

Example 1 was repeated except 20 parts of molybdenum trioxide was replaced by 20 parts of copper oxide to evaluate the concentration of carbon monoxide and nitrogen oxides in the gas generated in the tank. The burning pressure and period were of nearly same values as Example 1. The concentration of carbon monoxide in the gas generated in the tank was determined to be 1.4% by gas chromatography. The nitrogen oxides were not less than 2,000 ppm as determined by a detector tube.



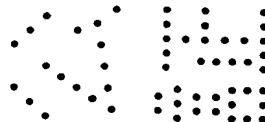
[Designation of Document] Abstract

[Abstract]

[Object] To provide a gas generant which decreases toxic components, in particular carbon monoxide and nitrogen oxides, in generated gas to a concentration practical as an air bag system for automobile.

[Structure] In the gas generant composition, nitrogen-containing organic compound such as a compound containing amino group or amido group or a tetrazole derivative and a oxygen-containing inorganic oxidizer such as potassium nitrate, strontium nitrate and potassium perchlorate are essential components. Therewith a molybdenum oxide catalyst of at least one selected from the group consisting of molybdenum dioxide, molybdenum trioxide, molybdic acid and ammonium molybdate is included.

[Selected Drawing] none



[Designation of the Document] Correction Data by Authority

[Corrected Document]

Patent Application

(Recognized and added Information)

[Applicant]

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[Selected Agent]

[Identification Number] 100076680

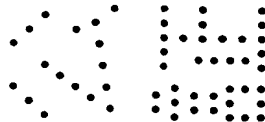
[Address or Residence] Furuya & Co.,  
Nihonbashi TM Building,  
1-8-11, Nihonbashi-Horidomecho,  
Chuo-ku, Tokyo

[Name] Takahiko MIZOBE

[Selected Agent]

[Identification Number] 100087642

[Address or Residence] Furuya & Co.,  
Nihonbashi TM Building,  
1-8-11, Nihonbashi-Horidomecho,  
Chuo-ku, Tokyo



【Name】

Satoshi FURUYA

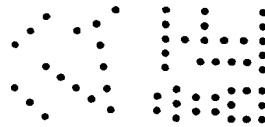
【Selected Agent】

【Identification Number】 100091845

【Address or Residence】 Furuya & Co.,  
Nihonbashi TM Building,  
1-8-11, Nihonbashi-Horidomecho,  
Chuo-ku, Tokyo

【Name】

Shinji MOCHIDA



Particulars of Applicant

Identification Number	[000002901]
1. Date of Changing	August 28, 1990
[Reasons of Changing]	New Registration
Address	1, Teppo-cho, Sakai-shi, Osaka
Name	Daicel Chemical Industries, Ltd.